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Isovaleric Aldehyde in the Synthesis of 4-Isobutyl-Substituted Pyridine-2(1*H*)-thiones, 4*H*-Pyrans, and 1,3-Cyclohexadiene

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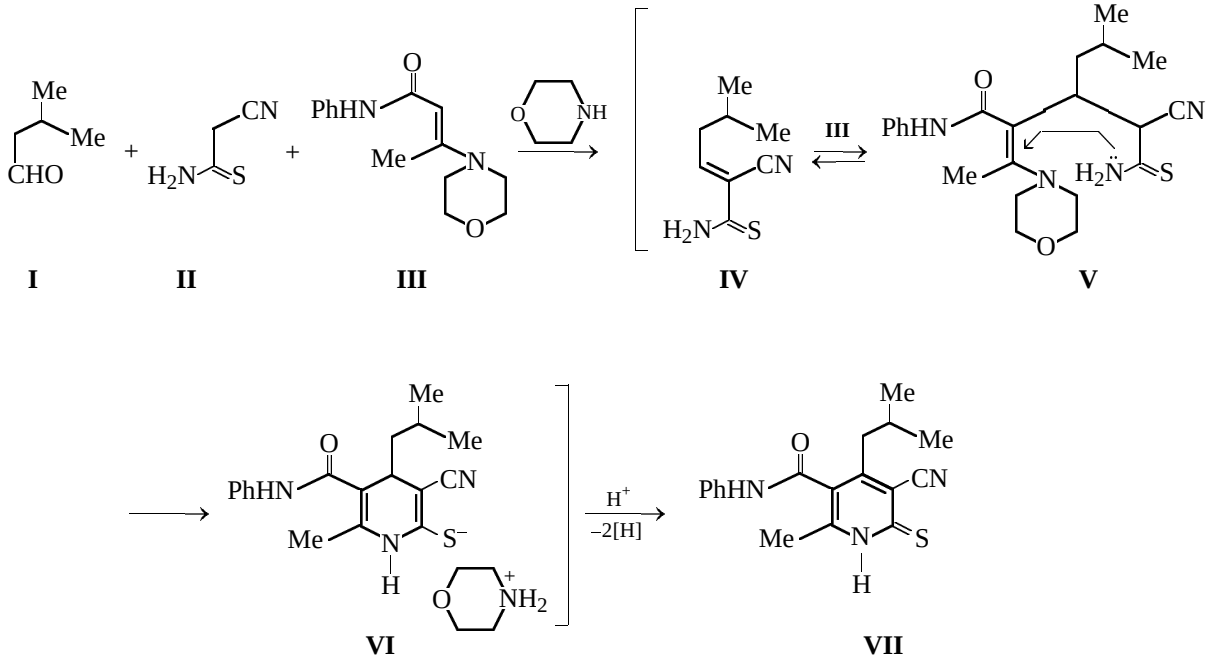
Abstract—Cyclocondensation of isovaleric aldehyde with various CH acids [benzoylacetonitrile, malononitrile, cyanothioacetamide, 4-hydroxycoumarin, resorcinol, 3-phenylpyrazol-5(1*H*)-one, 3-morpholinocrotonanilide] in the presence of amines yields isobutyl-substituted 4*H*-pyrans, 1,3-cyclohexadiene, and pyridine-2(1*H*)-thiones. The latter compounds were used in the synthesis of substituted 2-pyridino thioethers and thieno[2,3-*b*]pyridine.

Among alkyl-substituted pyridines there are central nervous system activators [1], fungicides, and agents for treating hyperlipoproteinemia [3], brain edema, asthma, shock, and other human diseases [4]. At the same time, alkyl-substituted pyridinechalcogenones and pyrans, which are also potentially bioactive [5, 6], are studied poorly [7].

Studies of the synthesis of alkyl-substituted heterocycles from aliphatic aldehydes and CH acids [8–10] showed that condensation of isovaleric aldehyde **I** with cyanoacetamide **II** and 3-morpholinocrotonanilide **III** in ethanol at 20°C in the presence of morpholine yields *N*-phenyl-4-isobutyl-6-methyl-2-thioxo-3-cyano-1,2-dihydropyridine-5-carboxamide **VII**. The reaction pathway apparently involves formation of alkene **IV** by the Knoevenagel reaction [11]. This is followed by alkylation of enamine **III** with olefin **IV**, which can be considered as Stork reaction [11]. The resulting adduct **V** undergoes intramolecular cyclocondensation to form substituted morpholinium 1,4-dihydropyridine-2-thiolate **VI**, transforming into pyridinethione **VII** on treatment with HCl.



I **II** **III** **IV** **V**

VI **VII**

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Table 1. Constants, yields, and elemental analyses of substituted pyridinethiones **VII** and **XI**, 2-pyridino thioethers **XIIIa** and **XIIIb**, thieno[2,3-*b*]pyridine **XIV**, pyrans **XXI, XXVII**, and **XXVIII**, 1,3-cyclohexadiene **XXXI**, and pentanodinitrile **XXXIV**

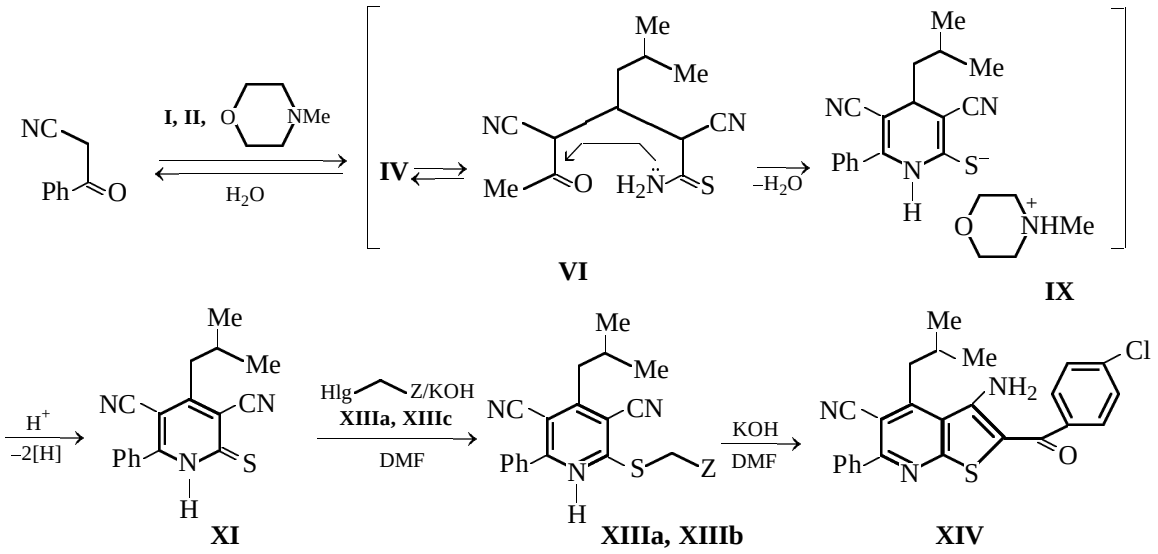
Comp. no.	Yield, %	mp, °C (solvent for) crystallization)	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
VII	82	243–245 (AcOH)	66.50	5.74	13.08	$C_{18}H_{19}N_3OS$	66.43	5.88	12.91
XI	66	220–222 (AcOH)	69.71	5.02	14.10	$C_{17}H_{15}N_3S$	69.60	5.15	14.32
XIIIa	93	168–169 (*i*-PrOH)	67.15	4.48	9.60	$C_{25}H_{20}ClN_3OS$	67.33	4.52	9.42
XIIIb	74	109–111 (MeOH)	65.69	5.08	11.37	$C_{20}H_{19}N_3O_2S$	65.73	5.24	11.50
XIV	80	263–265 (AcOH)	67.28	4.30	9.56	$C_{25}H_{20}ClN_3OS$	67.33	4.52	9.42
XXI	76	262–264 (EtOH)	61.95	5.92	16.88	$C_{17}H_{20}N_4OS$	62.17	6.14	17.06
XXVII	85	186–188[a] (EtOH)	68.70	6.52	11.56	$C_{14}H_{16}N_2O_2$	68.83	6.60	11.47
XXVIII	90	131–132 (EtOH)	69.70	6.85	8.41	$C_{19}H_{22}N_2O_3$	69.92	6.79	8.58
XXXI	77	141–143 (EtOH)	71.50	7.48	21.02	$C_{16}H_{20}N_4$	71.61	7.51	20.88
XXXIV	67	143–145 (*i*-PrOH)	60.51	7.42	14.96	$C_{19}H_{28}N_4O_4$	60.62	7.50	14.88

[a] Sublimes at 150°C.

With benzoylacetonitrile **VIII** used in the above reaction instead of enamine **III**, 4-isobutyl-2-thioxo-6-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile **XI** was obtained. Its 4-aryl-substituted isostructural analog was prepared previously by the reaction of arylmethylenebenzoylacetonitrile with cyanothioacetamide [12].

The probable scheme of formation of **XI** is shown below. CH Acid **VIII** adds by the Michael reaction [11] to Knoevenagel reaction product **IV**; the resulting adduct **IX** undergoes regioselective cyclocondensation into substituted *N*-methylmorpholinium 1,4-dihydropyridine-2-thiolate **X**. The latter product under the reaction conditions is protonated and oxidized (apparently, with atmospheric oxygen) to pyridinethione **XI**.

The structures of **VII** and **XI** were confirmed both by physicochemical and spectral data (Tables 1, 2) and by chemical transformations. In particular, the reactions of thione **XI** with compounds **XII** in basic media yield organic sulfides **XIII**. Treatment of **XIIIa** with an alkali yielded substituted thieno[2,3-*b*]pyridine **XIV**, which confirms the structure of thione **XI** and thioether **XIIIa** [13].



XII, Hlg = Br (**a**), Cl (**b**); **XII, XIII**, Z = 4-ClC_6H_4CO (**a**), COOMe (**b**).

Table 2. IR and ^{1}H NMR data for substituted pyridinethiones **VII** and **XI**, 2-pyridino thioethers **XIIIa** and **XIIIb**, thieno-[2,3-*b*]pyridine **XIV**, pyrans **XXI, XXVII**, and **XXVIII**, 1,3-cyclohexadiene **XXXI**, and pentanodinitrile **XXXIV**

Comp. no.	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm (*J*, Hz)			
	ν(C≡N)	ν(NH$_2$), δ(NH$_2$), ν(C=O)	CH(*Me*)$_2$, d	C*H*(Me)$_2$, m	CH$_2$	other signals
VII[a]	2230	3300, 1666	0.89 (*J* 8.40)	2.00	2.60 d (*J* 7.95)	2.41 s (3H, C^{6}Me), 7.13–7.63 m (5H, Ph), 10.48 br.s (1H, NHCO)
XI[a]	2232 sh	–	1.04 (*J* 8.48)	2.12	2.73 d (*J* 8.14)	7.51–7.73 m (5H, Ph)
XIIIa	2228 sh	1712	1.00 (*J* 8.39)	2.10	2.87 d (*J* 8.05)	5.01 s (2H, SCH$_2$), 7.30 d and 8.03 d (2H each, C$_6$H$_4$, *J* 8.3), 7.41–7.69 m (5H, Ph)
XIIIb	2227	1740	1.02 (*J* 8.20)	2.13	2.84 d (*J* 8.11)	3.60 s (3H, MeO), 4.25 s (2H, SCH$_2$), 7.69 m (3H, Ph), 7.88 m (2H, Ph)
XIV	2225	3214, 3352, 3418, 1670, 1738	1.14 (*J* 8.18)	2.09	2.79 d (*J* 8.10)	7.48 d and 8.15 d (2H each, C$_6$H$_4$, *J* 8.0), 7.60–7.92 m (5H, Ph), 8.17 br.s (2H, NH$_2$)
XXI	–	3214, 3300, 3452, 1647	0.68 (*J* 8.27)	1.24	1.93 m	3.84 t (1H, C^{4}H, *J* 9.15), 7.02–7.66 m (9H, NH$_2$, CSNH$_2$, Ph), 11.82 br.s (1H, N^{2}H)
XXVII	2200	3150, 3196, 3335, 1644	0.89 (*J* 8.30)	1.65	1.34 m	3.36 d (1H, C^{4}H, *J* 6.20), 6.34 s (1H, C^{8}H), 6.07 d (1H, C^{5}H, *J* 9.10), 6.68 br.s (2H, NH$_2$), 6.94 d (1H, C^{6}H), 9.55 br.s (1H, OH)
XXVIII	2199	3211, 3332, 3420, 1648, 1688	0.95 m[b]	1.90	1.47 d.d (*J* 7.12)	0.95 m (2H, CH$_2$C*H*$_3$),[b] 3.30 t (1H, C^{4}H, *J* 5.64), 3.94 q (2H, OCH$_2$, *J* 7.10), 6.54 br.s (2H, NH$_2$), 7.38 br.s (5H, Ph)
XXXI	2210, 2254	3212, 3450, 1650	0.95 d (*J* 8.14)	1.58	1.40 m	1.14 d [6H, (CH$_3$)$_2$, *J* 8.15], 2.19 m [1H, CH(Me)$_2$], 3.10 t (1H, C^{5}H, *J* 7.12), 5.22 s (1H, C^{3}H), 7.46 br.s (2H, NH$_2$)
XXXIV	2249	1676	0.91 d, 0.98 d (*J* 8.33)	1.76	1.54 m	3.20–3.78 m [16H, (C$_4$H$_8$NO)$_2$], 4.29 d and 4.38 d [1H each, (CHCN)$_2$], 4.50 m (1H, CH)

[a] The N^{6}H proton signal is not observed, probably besause of deuterium exchange. [b] The signals overlap.

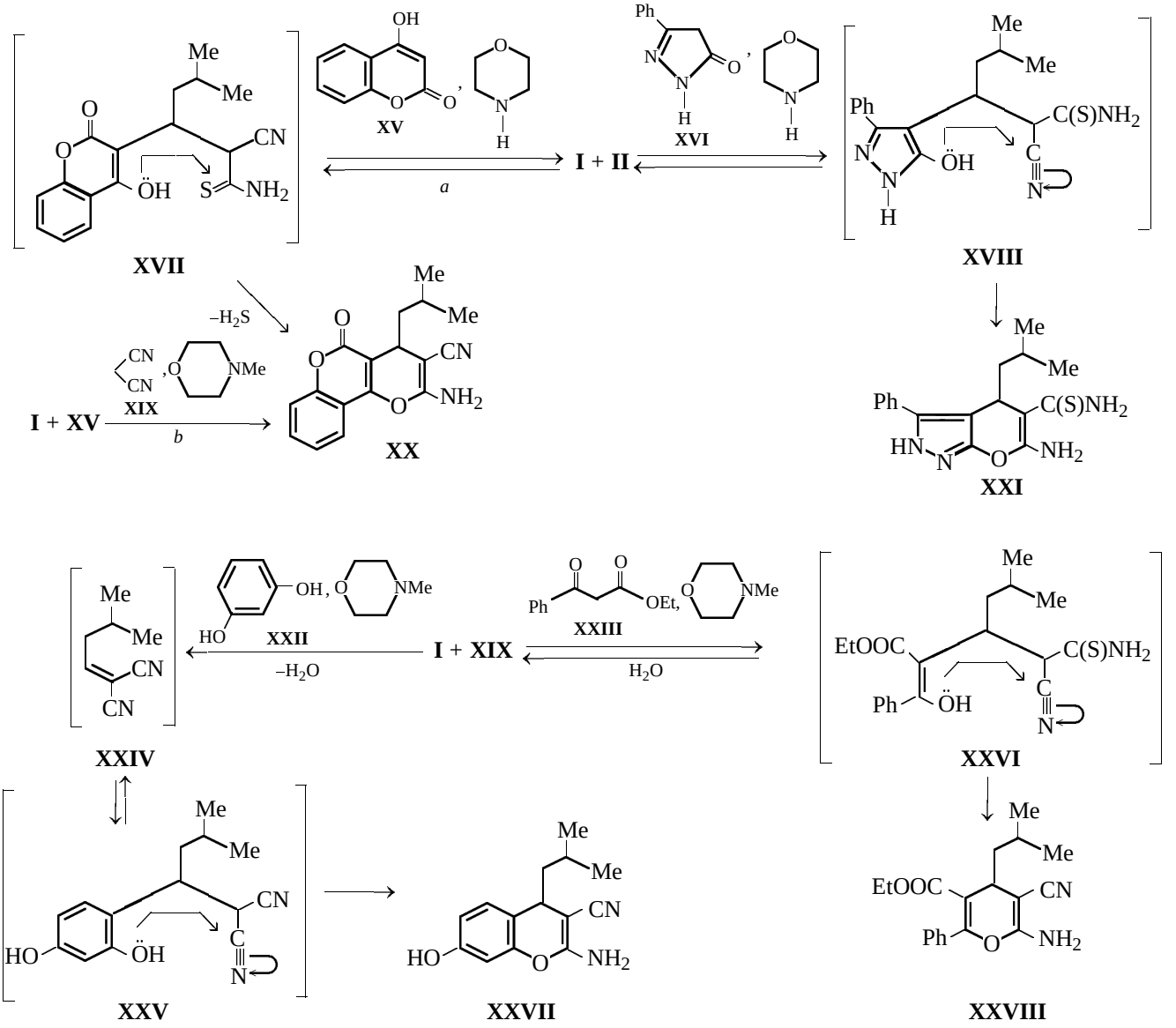
The three-component condensation of isovaleric aldehyde **I**, cyanothioacetamide **II**, and 4-hydroxycoumarin **XV** in ethanol at 20°C in the presence of morpholine yields 2-amino-4-isobutyl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile **XX** (method *a*). With 3-phenylpyrazol-5(1*H*)-one **XVI** used as the third component instead of **XV**, 6-amino-4-isobutyl-3-phenyl-2*H*,4*H*-pyrano[2,3-*c*]pyrazole-5-carbothioxamide **XXI** is obtained. It is reasonable to assume the formation of the corresponding Michael adducts **XVII** and **XVIII** in the course of these reactions. It is known that, in three-component condensation of aromatic aldehydes, cyanothioacetamide, and 4-hydroxycoumarin in the presence of amines, adducts of type **XVII** can be isolated and characterized as ammonium salts [14].

The structures of **XX** and **XXI** were confirmed by IR, ^{1}H NMR, and mass spectra (Table 2), and also by independent synthesis from isovaleric aldehyde **I**, malononitrile **XIX**, and 4-hydroxycoumarin **XV** (method *b*) [15].

The condensation of isovaleric aldehyde **I** with malononitrile **XIX** and resorcinol **XXII** in ethanol in the presence of *N*-methylmorpholine yields 2-amino-

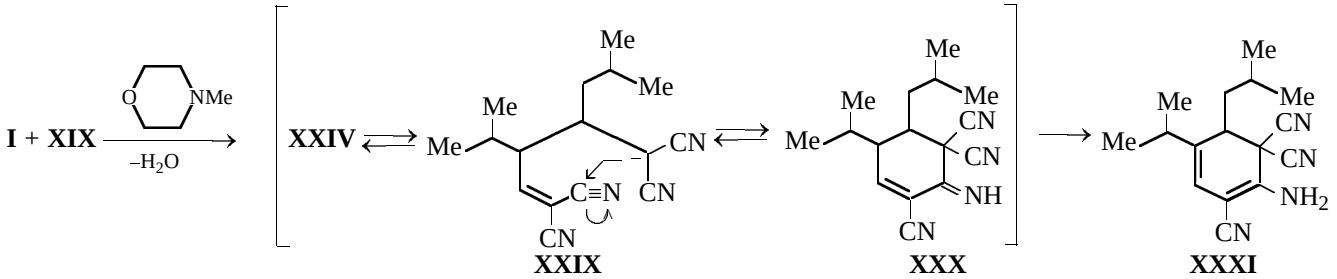
7-hydroxy-4-isobutyl-4*H*-chromene-3-carbonitrile **XXVII**. Its isostructural analogs can be used for protection of agricultural plants from the damage caused by herbicides [16] and as antiasthmatic agents [17].

With ethyl 3-oxo-3-phenylpropanoate **XXIII** used instead of resorcinol **XXII** in this reaction, ethyl 6-amino-4-isobutyl-2-phenyl-5-cyano-4*H*-pyran-3-carboxylate **XXVIII** is obtained.



Compounds **XXVII** and **XXVIII** are apparently formed via intermediate isopentylidenemalononitrile **XXIV** to which CH acids **XXII** and **XXIII** add by the Michael reaction. The corresponding adducts **XXV** and **XXVI** undergo intramolecular cyclization to give, respectively, **XXVII** and **XXVIII**. This reaction pathway is confirmed by two-component cyclization of isovaleric aldehyde **I** with malononitrile **XIX**. This reaction yielded 1-amino-5-isobutyl-4-isopropyl-1,3-cyclohexadiene-2,6,6-tricarbonitrile **XXXI** as a result of Michael dimerization of alkene **XXIV** into adduct **XXIX** followed by the Thorpe–Ziegler [18] transformation into imine **XXX**. The latter is stabilized in the form of substituted 1,3-cyclohexadiene **XXXI**.

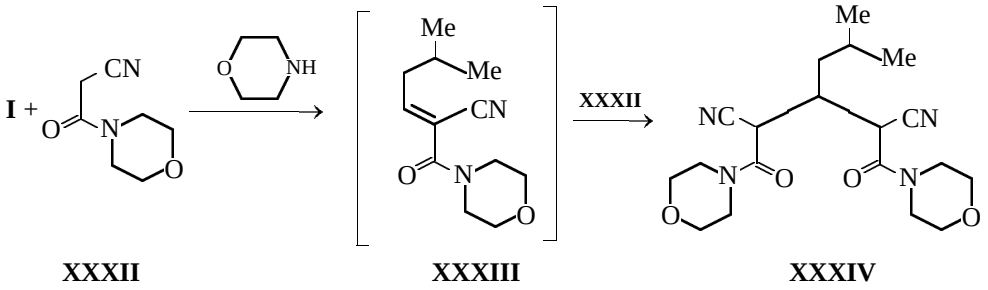
The structure of **XXXI** is confirmed by the spectral data (Table 2). Its mass spectrum contains a molecular peak at *m/z* 268, in accordance with the "nitrogen



rule" [19]. The high intensity of the $[M]^+$ peak (see Experimental) at the ionizing electron energy of 70 eV is typical of compounds with the high formal degree of unsaturation [20].

The IR spectrum contains stretching vibration bands of a conjugated nitrile group at 2210 cm^{-1} and a nonconjugated nitrile group at 2254 cm^{-1}, and also stretching (3212, 3450 cm^{-1}) and bending (1650 cm^{-1}) vibration bands of the amino group. The ^1H NMR spectrum of **XXXI** contains characteristic signal of amino group protons as a broadened singlet at δ 7.46 ppm, a C^3H proton singlet at δ 5.22 ppm, and characteristic signals of the protons of aliphatic substituents and C^5H proton (Table 2).

The two-component condensation of isovaleric aldehyde **I** with 3-morpholino-3-oxopropanonitrile **XXXII** in the presence of morpholine follows the Knoevenagel reaction pattern and yields alkene **XXXIII**. However, we failed to isolate it because of easy subsequent Michael addition of CH acid **XXXII** to **XXXIII** under the reaction conditions. Adduct **XXXIV** formed in the process is stable; it was isolated and characterized (Tables 1, 2).



The yield of **XXXIV** is the highest at **I** : **XXXII** = 1 : 2, which confirms the suggested reaction mechanism. Similar adducts were obtained previously by condensation of aliphatic aldehydes with cyanoacetamide [21]. At the same time, sulfur analogs of adducts **XXXIV** cannot be prepared because of their easy transformation into 5-amino-8-isobutyl-7-isopropyl-6-thiocarbamoyl-4-cyano-2-azabicyclo[2.2.2]oct-5-ene-3-thione [9, 22].

EXPERIMENTAL

The IR spectra were taken on an IKS-29 spectrometer (mulls in mineral oil). The ^1H NMR spectra were taken on Bruker WP-100SY (100 MHz, compounds **VII**, **XIIIa**, **XXVII**), Gemini-200 (199.975 MHz, compounds **XX**, **XXVIII**), Bruker WM-250 (250.13 MHz, compounds **XIV**, **XXI**, **XXXI**), Bruker AM-300 (300.13 MHz, compounds **XI**, **XXXIV**), and Bruker DR-500 (500.13 MHz, compound **XIIIb**) spectrometers (solutions in DMSO-d_6, internal reference TMS). The mass spectra were recorded on a Kratos MS-890 spectrometer (70 eV). The melting points were determined with a Koefler unit. The reaction progress was monitored by TLC (Silufol UV-254, acetone–hexane, 3 : 5, development with iodine vapor).

***N*-Phenyl-4-isobutyl-6-methyl-2-thioxo-3-cyano-1,2-dihydropyridine-5-carboxamide VII.** A drop of morpholine was added to a mixture of 1.08 ml of isovaleric aldehyde **I** and 1.0 g (10 mmol) of cyanothioacetamide **II** in 15 ml of ethanol at 20°C. The mixture was stirred for 10 min. Then 2.46 g of enamine **III** was added, and the mixture was stirred for 30 min and allowed to stand at room temperature for 24 h. After that, the mixture was diluted with 10% HCl to pH 5

and allowed to stand for 48 h. The precipitate of pyridinethione **VII** (Tables 1, 2) was filtered off and washed with water, ethanol, and hexane.

4-Isobutyl-2-thioxo-6-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile XI. *N*-Methylmorpholine (1.1 ml) was added to a suspension of 1.0 g of cyanothioacetamide **II** in 15 ml of ethanol at 20°C. The mixture was stirred for 8 min until a homogeneous solution formed. Then 1.08 ml of isovaleric aldehyde **I** was added, and the mixture was stirred for 10 min. After that, 1.45 g of **VIII** was added, and the mixture was stirred for an additional 30 min. After standing for a day, the mixture was diluted with 10% HCl and left for 48 h at room temperature. The precipitate of pyridinethione **XI** (Tables 1, 2) was separated and washed with water, ethanol, and hexane. Mass spectrum, *m/z* (I_{rel}, %): 295 (2) $[M + 2]^+$, 294 (11) $[M + 1]^+$, 293 (40) $[M]^+$, 292 (63) $[M - 1]^+$, 279 (7), 278 (25), 253 (6), 252 (17), 251 (100), 250 (15), 224 (7), 207 (9), 77 (13).

4-Isobutyl-6-phenyl-2-(*Z*-methylsulfanyl)pyridine-3,5-dicarbonitriles XIIIa and XIIIb. To a solution of 2.93 g of pyridinethione **XI** in 8 ml of DMF, we added successively 5.6 ml of 10% aqueous KOH and 100 ml of appropriate halide **XII**. The mixture was stirred for 30 min and diluted with an equal volume of water. The precipitate of **XIIIa** or **XIIIb** (Tables 1, 2) was separated and washed with water, ethanol, and hexane.

3-Amino-4-isopropyl-6-phenyl-2-(4-chlorophenylbenzoyl)thieno[2,3-*b*]pyridine-5-carbonitrile XIV. To a solution of 4.46 g of **XIIIa** in 15 ml of DMF, we added with stirring 5.6 ml of 10% aqueous KOH. The mixture was stirred for 1 h and then gradually diluted with an equal volume of water. The precipitate of **XIV** (Tables 1, 2) was filtered off and washed with water, ethanol, and hexane.

2-Amino-4-isobutyl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]-chromene-3-carbonitrile XX. *a*. A 0.87-ml portion of morpholine was added with stirring at 20°C to a mixture of 1.08 ml of isovaleric aldehyde **I** and 1.0 g of cyanothioacetamide **II** in 15 ml of ethanol. The mixture was stirred for 5 min, after which 1.62 g of 4-hydroxycoumarin was added, and the mixture was stirred for 15 min and allowed to stand for a day. The finely crystalline colorless precipitate of **XX** was filtered off and washed with ethanol and hexane. Yield 74%. As judged from the melting point, chromatographic data, and ^{1}H NMR and IR spectra, the product is identical to that obtained by method *b* [15].

6-Amino-4-isobutyl-2*H*,4*H*-pyrano[2,3-*c*]pyrazole-5-carbothioxamide XXI was prepared similarly to **XX** (method *a*) using **XVI** instead of **XV**. The characteristics of **XXI** are given in Tables 1 and 2. Mass spectrum, *m/z* (I_{rel}, %): 330 (7) $[M + 2]^+$, 328 (9) $[M]^+$, 326 (10) $[M - 2]^+$, 253 (64), 229 (21), 228 (79), 214 (20), 213 (82), 186 (15), 185 (24), 173 (85), 161 (26), 160 (100), 144 (20), 129 (28), 115 (27), 104 (30), 103 (87), 91 (14), 77 (85), 58 (92).

2-Amino-7-hydroxy-4-isobutyl-4*H*-chromene-3-carbonitrile XXVII. To a solution of 1.08 ml of isovaleric aldehyde **I** in 15 ml of ethanol, we added 0.66 g of malononitrile **XIX** and three drops of *N*-methylmorpholine; the mixture was stirred for 10 min. Then 1.10 g of resorcinol **XXII** was added, and the mixture was stirred for 30 min and left at room temperature. In 3 days, colorless crystals of **XXVII** (Tables 1, 2) formed, which were filtered off and washed with ethanol and hexane.

Ethyl 6-amino-4-isobutyl-2-phenyl-5-cyano-4*H*-pyran-3-carboxylate XXVIII was prepared similarly to **XXVII**, with ethyl 3-oxo-3-phenylpropanoate **XXIII** used instead of resorcinol **XXII**. The characteristics of **XXVIII** are given in Tables 1 and 2. Mass spectrum, *m/z* (I_{rel}, %): 326 (4) $[M]^+$, 271 (18), 269 (100), 241 (18), 197 (5), 105 (27), 77 (14), 41 (6).

1-Amino-5-isobutyl-4-isopropyl-1,3-cyclohexadiene-2,6,6-tricarbonitrile XXXI. A mixture of 1.08 ml of isovaleric aldehyde **I**, 0.66 g of malononitrile **XIX**, and three drops of *N*-methylmorpholine in 15 ml of ethanol was stirred for 1 h and allowed to stand for a day. A colorless crystalline precipitate of **XXXI** (Tables 1, 2) formed, which was separated and washed with ethanol and hexane. Mass spectrum, *m/z* (I_{rel}, %): 270 (8) $[M + 2]^+$, 269 (22) $[M + 1]^+$, 268 (87) $[M]^+$, 254 (10), 253 (25), 226 (25), 225 (76), 212 (28), 211 (95), 198 (28), 197 (95), 186 (30), 184 (69), 171 (30), 170 (96), 169 (100), 156 (60), 145 (28), 144 (96), 119 (20), 109 (18), 79 (8), 69 (17).

3-Isobutyl-2,4-di(morpholinocarbonyl)pentanodinitrile XXXIV. A mixture of 1.08 ml of isovaleric aldehyde **I**, 3.08 g of 3-morpholino-3-oxopropanonitrile **XXXII**, and three drops of morpholine in 15 ml of ethanol was stirred for 25 min at room temperature to obtain a homogeneous solution. The mixture was allowed to stand at room temperature for 48 h. The precipitate was filtered off and washed with ethanol and hexane. Compound **XXXIV** (Tables 1, 2) was thus obtained as a colorless powder. Mass spectrum, *m/z* (I_{rel}, %): 376 (14) $[M]^+$, 308 (10), 290 (43), 223 (100), 154 (19), 114 (25), 86 (27), 70 (51), 56 (78), 41 (63).

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